DETERMINATION OF THE BURNING CHARACTERISTICS OF OF A SLICK OF OIL ON WATER

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ABSTRACT

The burning rate of a slick of oil on a water bed is characterized by three distinct processes, ignition, flame spread and burning rate. Although all three processes are important, ignition and burning rate are critical. The former, because it defines the potential to burn and the latter because of the inherent possibility of boilover. Burning rate is calculated by a simple expression derived from a one-dimensional heat conduction equation. Heat feedback from the flame to the surface is assumed to be a constant fraction of the total energy released by the combustion reaction. The constant fraction (χ) is named the burning efficiency and represents an important tool in assessing the potential of in-situ burning as a counter-measure to an oil-spill. By matching the characteristic thermal penetration length scale for the fuel/water system and an equivalent single layer system, a combined thermal diffusivity can be calculated and used to obtain an analytical solution for the burning rate. Theoretical expressions were correlated with crude oil and heating oil, for a number of pool diameters and initial fuel layer thickness. Experiments were also conducted with emulsified and weathered crude oil. The simple analytical expression describes well the effects of pool diameter and initial fuel layer thickness permitting a better observation of the effects of weathering, emulsification and net heat feedback to the fuel surface. Experiments showed that only a small fraction of the heat released by the flame is retained by the fuel layer and water bed (of the order of 1%). Ignition has been studied to provide a tool that will serve to assess a fuels ease to ignite under conditions that are representative of oil spills. Two different

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techniques are used, piloted ignition when the fuel is exposed to a radiant heat flux and flash point as measured by the ASTM D56 Tag Closed Cup Test. Two different crude oils were used for these experiments, ANS and Cook Inlet. Crude oils were tested in their natural state and at different levels of weathering, showing that piloted ignition and flash point are strong functions of weathering level.

Keywords: Oil spill, burning rate, ignition, crude oil, weathering, emulsification, pool fire

INTRODUCTION

The burning of oil in water is of great interest as a result of off-shore exploration, production and transportation of petroleum. This combustion phenomenon may constitute a hazard, i.e. and accidental burning slick drifting towards a platform, but it may also serve as a measure to minimize the environmental damage of an oil spill (Twardus and Brzustowski (1981), Evans et al. (1990)).

The available information on this phenomenon is quite limited. Although great effort has been devoted to the understanding of pool fires [Drysdale, 1985] and flame spread over liquid pools (Williams (1985), Ross (1994), Glassman and Dryer (1981)) the specific issues related to a fuel burning over a water bed have deserved little attention. Most of the work being related to fires in fuel tanks and the phenomena commonly referred as "boilover" (Ito et al. (1992), Arai et al. (1990)). Only a few studies have dealt with the burning of a thin layer of fuel on a water bed. A good summary of existing knowledge is provided by Evans et al. (1990).

In an attempt to provide an adequate methodology for ignition of oil-spills a review of the ignition methods commonly used for oil spill clean-up was provided in the proceedings edited by Jason (Jason, 1989). Ignition source temperatures and successful ignition conditions have also been a subject of interest (Bech et al. (1990), Thompson et al. (1979)). A cone calorimeter was used by Putorti et al. (1994) to quantify the heat flux necessary to accomplish ignition of different fuel. In this work emphasis was given to the effects of weathering and emulsification on ignition. A review of most of the work that relates to oil-spill combustion studies is provided by Walavalkar and Kulkarni (1996).

Assuming that the fuel layer is ignitable an important concern is thin layer boil-over. The term "boilover" has been usually applied to a fire scenario in which an open top tank containing burning crude oil, after a long period of quiescent burning, shows a sudden increase in fire intensity associated with the expulsion of burning oil from the tank (Henry and Klem (1983)). The term boilover has also been applied to the burning of thin layers of fuel on the surface of water in order to limit the spread of oil after an accident (Koseki and Mulholland, 1991). This scenario is commonly referred as thin layer boil-over. Although somehow different in nature, both cases result from the onset of boiling nucleation at the fuel/water interface and therefore, the time from ignition to the onset of boilover correlates well with the time needed for the thermal wave to reach the water (Garo et al., 1994)).

The problems linked to thin layer boilover are related to the uncontrolled nature of the combustion process and the total fraction of fuel consumed during the burning process. The total fraction of fuel burnt before boilover increases with the fuel layer thickness if the layer is thinner than 10 mm and remains constant for thicker layers (Alramdhan et al., 1990). The amount of fuel consumed after the onset of boilover dramatically decreases with the fuel thickness (Koseki et al. 1991). Thick fuel layers lead to a "hot zone" formation that results in explosive boilover and low fuel consumption,

thinner layers follow a smoother transition between pool like burning and boilover which leads to high fuel consumption.

Geometrical considerations that pertain to the burning rate are of great importance when considering the use of burning for oil spill cleanup. If the oil spill is not contained, the fuel layer thickness decreases until self-sustained burning is no longer possible. Typical values of the order of 0.5 mm have been identified as a minimum thickness for self-sustain burning (Arai et al. (1990), Garo et al. (1994), Alramadhan et al. (1990)). The effect of fuel thickness, pool diameter and fuel boiling point on the burning rate has also been studied by Garo et al. (1994, 1996) who observed that the burning rate does not depend on the initial fuel layer thickness for fuel layers thicker than 10 mm and decreases for thinner layers.

One of the first attempts to model this type of problem was made by Twardus and Brzustowski (1981), who developed a simple one-dimensional model to describe the combustion of oil slicks on water. This model describes the burning process as that of a pool fire with a heat loss term from the fuel to the water underneath. Heat losses from the fuel towards the water will increase as the fuel layer thickness decreases, therefore, a minimum thickness for self-sustained burning can be established. In a later model Brzustowski and Twardus (1982) incorporated the effects of radiative absorption in the fuel and the effect of tilting by the wind. A more realistic model that incorporates radiative feedback and the effects of turbulent buoyant motion was subsequently developed by Alramadhan et al. (1990), emphasis was given to the regressing surface and the gas phase and no account for heat transfer towards the water bed was made. Although these simple theories obtain expressions for the burning rate and minimum thickness for self-sustained burning, they all fail to describe the evolution of the burning rate as the fuel thickness decreases below 10 mm.

An issue of concern when determining the adequate counter-measure to be used in a specific oil-spill scenario is the efficiency of the clean-up process. Different factors such as fuel layer thickness, weathering or formation of emulsions, have a significant effect. As a norm large scale tests have been used to provide an estimate of the efficiency of the counter-measure (Twardus and Brzustowski (1981), Evans et al. (1990), Jason (1989)). The prohibitive cost of this methodology requires an examination of bench scale procedures that will provide adequate estimates of how the different processes occurring in an oil-spill scenario will affect the burning efficiency. The present work does not attempt to be a substitute to large scale testing, but just a complement that would lead to reduction of the ultimate number of tests necessary to predict the efficiency of in-situ burning as a counter-measure for an oil spill.

In this work a simple heat conduction models are used to describe the pre-boil over ignition and burning rate of crude oil and heating oil. The diameter dependency of the heat released by the flame is determined from an existing correlation for pool fires (Drysdale (1985), Pipkin and Ssliepcevich (1964), McCaffrey (1979), Cox (1995)). Assuming that a specific fraction of the heat released (χ) is fed back to the fuel surface an expression for the regression rate can be obtained. The results from the model are then compared with experimental results for different fuels to validate the independence of the efficiency parameter on the different parameters of the problem. The parameters varied are pool diameter, fuel layer thickness, weathering level and the percentage of water emulsified in the fuel. The model is only valid for the range where the heat release correlation is valid, therefore bench scale experiments should be conducted under those conditions. Gritzo et al. (1996) noted that as the pool diameter increases burning conditions change and radiation blockage towards the surface influences the burning rate. The value for the efficiency can, thus, not be extrapolated to large-scale burns, but can be used to provide a

relative ranking among fuels. Ignition is studied using ASTM standard test methods slightly modified to better treat the fuels of interest. The description of the methodology is provided in reference (Wu et al. (2000)) and details of the standards in reference (ASTM (1994)).

BURNING RATE FORMULATION

Heat release rate from a pool fire has been documented extensively (Drysdale (1985), Pipkin and Ssliepcevich (1964), McCaffrey (1979), Cox (1995)) and it has been found that the expression

$$\dot{Q} = \rho_\infty C_p (T_\infty g (T_f - T_\infty))^{1/2} d^{5/2} \qquad (1)$$

correlates well with values measured experimentally (Alramadhan et al. (1990), Mudan and Croce (1995)). The total heat release from the combustion process is denoted by $\dot{Q}$ [W], C_p [J/kgK] is the specific heat at constant pressure and ambient temperature for air, T_∞ is the ambient temperature, T_f is and average flame temperature (for this work $T_f \approx 1100$ K (Cox, 1995)), g is the acceleration of gravity (g=9.81 m/s^2), d (diameter of the fuel pool) is the characteristic length scale, ρ [kg/m^3] is the density of the air at ambient temperature and the sub-index ∞ stands for ambient conditions.

The net heat fed back per unit area to the fuel represents a small fraction of the total heat release, this fraction (χ) has been found to be independent of the pool diameter (Mudan and Croce, 1995) and thus, the heat flux per unit area reaching the surface can be expressed as

$$\dot{q}''_S = \chi \frac{4 \rho_\infty C_p (T_\infty g (T_f - T_\infty))^{1/2} d^{1/2}}{\pi} \qquad (2)$$

If conduction is assumed to be the dominant heat transfer mechanism and if the thermal wave has not reached the fuel/water interface the fuel can be considered as semi-infinite and an expression for the temperature as a function of time and position can be obtained. This treatment can also be used when fuel and water have similar thermal diffusivities (Arai et al. 1990, Garo et al., 1994)). If fuel and water have significantly different thermal diffusivities and the thermal wave has already reached the fuel/water interface, fuel and water layers need to be treated independently. The water can still be assumed as semi-infinite but the fuel layer needs to be treated as a layer of finite thickness.

Radiation through the fuel layer can be of importance (Alramadhan et al. (1990), Brzustowski and Twardus, 1982) but for the fuels of interest it has been demonstrated that most of the radiative heat flux is absorbed very close to the surface (Garo et al., 1996). Natural convection inside the fuel and water layers can significantly enhance heat transfer close to the fuel surface but seems to affect only weakly steady burning for highly viscous fuels (Ross, 1994). The importance of natural convection decreases with viscosity and its effects can be neglected for those fuels relevant to this study, this is not the case for less viscous fuels (i.e. octane, xylane, etc.) (Garo et al., 1996). For simplicity, this analysis will assume conduction to be the dominant heat transfer mechanism.

General Statements

A schematic of the problem to be studied is presented in Figure 1. Assuming no convective motion and that radiation is fully absorbed at the surface, the following energy balance can be made at $y=y_S(t)$

$$\dot{q}''_S = H_V \rho_F r(t) + \dot{q}''_C \qquad (3)$$

where $\dot{q}''_C = -\lambda_F \left.\frac{\partial T}{\partial y}\right|_{y=y_S(t)}$ is the heat conducted into the fuel layer, H_V is the latent heat of vaporization, t is a specific time, T is the temperature, ? is the thermal conductivity, $r(t) = \frac{\partial}{\partial t}(y_S(t))$ is the regression rate, $y_S(t)$ is the location of the fuel surface at a specified time, and the sub-index F stands for fuel. For the entire analysis, it is assumed that the ignition source brings the surface temperature to T_S (vaporization temperature of the fuel) instantaneously. The vaporization temperature is considered to remain constant throughout the entire burning time.

Under this assumptions the regression rate (r(t)) is given by the following equation

$$r(t) = \frac{\dot{q}''_S - \dot{q}''_C}{H_v \rho_F} \qquad (4)$$

where the net heat flux is given by equation (2) and the latent heat of vaporization and density are properties of the fuel. The only unknown is the heat conducted into the surface and evaluation of this term will be the subject of the following sections.

Heat Conducted Into the Fuel Layer ($\dot{q}''_C$)

Once ignition occurs the fuel and water bed undergo a transient heating process that will eventually lead to steady regression rate. The regression rate corresponding to the transient period has been previously studied by many authors (Quintiere and Iqbal, 1994, Steckler et al., 1991, Butler, 1996)). The ignition process needs to be well characterized to be able to determine the time dependency of the heat transfer into the fuel/water bed. Quintiere and Iqbal (1994) and Steckler et al. (1991) proposed models that describe the transient stages of the surface regression for thermoplastic materials subject to a constant external heat flux previous to piloted ignition. In these particular cases the fuel was a single layer and the time dependency of heating process could be precisely traced since the sample at ambient temperature was suddenly exposed to the external heat flux. Butler (1996) introduces a finite layer fuel on a semi-infinite bed and solves the transient process analytically. Again, the fuel was subject to sudden heating. In all these analytical studies it was shown that a short transient process is followed by an almost steady regression rate.

The ignition protocol corresponding to the experimental data available for fuels characteristic of oil-spill scenarios does not correspond to the well controlled conditions presented in the above referred models. In all cases the regression rate is presented as an average value corresponding to the quasi-steady process. It is clear that as the fuel layer is consumed the regression rate is going to drop due to

the effect of the water sub-layer, but the quasi-steady period could be used to extract the fuel properties.

In summary, the regression rate will undergo three stages, an initial transient stage were the regression rate increases with time as the fuel/water bed undergoes pre-heating. This period is very short (Quintiere and Iqbal, 1994, Steckler et al., 1991, Butler, 1996) and can be neglected for the purpose of this work. The initial stage is followed by a quasi-steady regime where the regression rate attains an almost constant value, experimental data available and that collected in the present work corresponds to this period. This period is ideal to obtain a simple expression that will serve to quantify the efficiency of the burning process and will be the subject of the present analysis. When the fuel layer reaches a critical thickness the regression rate will decrease due to the heat sink effect of the water sub-layer.

A steady regression rate can be attained before or after the thermal front has reached the fuel/water interface. In the former case the fuel acts as a thermally thick material and a single a one-dimensional heat conduction equation can be used to derive the value of $\dot{q}''_C$. In the latter case, the fuel is thermally thin so the water contribution needs to be included. Two energy equations will be necessary to obtain $\dot{q}''_C$. The two cases will be treated and presented independently the former will be referred to as a *"One-Dimensional Single Layer Conduction Model"* and the latter as *"One-Dimensional Two Layer Conduction Model."*

One-Dimensional Single Layer Conduction Model

This analysis is an extension of the works of Arai et al. (1990) and Garo et al. (1996). Details of the formulation will not be presented here and therefore, the reader is referred to these works for further information.

The heat conduction equation for a one-dimensional semi-infinite element is given by:

$$\frac{\partial^2 T}{\partial y^2} = \frac{1}{\alpha_F}\frac{\partial T}{\partial t} \qquad (5)$$

with initial condition at

$t=0, \quad T = T_\infty$

and boundary conditions

$y = y_S(t), \quad T = T_S$

$y \to \infty, \quad T = T_\infty$

if α_F is the thermal diffusivity of the fuel and "r" is assumed to be constant then the following expression for the temperature distribution can be obtained

$$\frac{T - T_\infty}{T_S - T_\infty} = \exp(-\frac{r}{\alpha_F}(y - y_S(t))) \qquad (6)$$

this expression will be accurate if the thermal diffusivity of the fuel is approximately equal to the thermal diffusivity of water ($\alpha_F \approx \alpha_W$) or for a time period "t" earlier than the characteristic time for the thermal front to reach the fuel/water interface.
Knowing the temperature distribution it is possible to calculate $\dot{q}''_C$ and by substituting in equation (4) an expression for the average regression rate can be calculated.

One-Dimensional Two Layer Conduction Model

The thermal diffusivity of water is significantly bigger than that of the fuels of interest (Table 1) and as soon as the thermal wave reaches the fuel/water interface, the water bed starts acting like a heat sink. A full description of this scenario is given by the following set of differential equations and boundary conditions.

$$\frac{\partial^2 T}{\partial y^2} = \frac{1}{\alpha_F}\frac{\partial T}{\partial t} \qquad (7)$$

$$\frac{\partial^2 T}{\partial y^2} = \frac{1}{\alpha_W}\frac{\partial T}{\partial t} \qquad (8)$$

with initial condition at

t=0, $T = T_\infty$

and boundary conditions

$$y = y_S(t), T = T_S$$

$$y = 0, -\lambda_F \left.\frac{\partial T}{\partial y}\right|_{y=0^-} = -\lambda_W \left.\frac{\partial T}{\partial y}\right|_{y=0^+}$$

$$y \to \infty, T = T_\infty$$

The use of equation (4) and a numerical solution of the equations (7) and (8) is necessary to obtain the corresponding temperature distributions and regression rate. As mentioned before, the data available in the literature generally provides only average regression rates. Therefore, only an order of magnitude comparison will be possible. A simplified approach that incorporates the main physical characteristics and provides a closed form solution to r(t) is, thus, used to solve the above system of equations in place of a numerical solution.

The average regression rate and characteristic velocity of the thermal wave are very similar and have been reported of the order of 10^{-5} m/s (Garo et al., 1994). Providing a very large time for thermal relaxation (of the order of 1000 sec.), the relative displacement of both waves is very small. This particular characteristic makes it possible to solve only the two-layer steady state equation at each stage

of the regression process. The steady-state equation leads to linear temperature profiles and, therefore, an equivalent thermal diffusivity can be obtained.

The equivalent thermal diffusivity results from matching the thermal penetration distance through a two-layer bed with thermal diffusivities α_F and α_W and the thermal penetration distance in one single layer of thermal diffusivity α_{EQ}. The characteristic length for the fuel layer will be $y_{S,i}$ and the average regression rate, r, is assumed to be constant. From equations (7) and (8):

$$\alpha_{EQ} = \frac{r\, y_{S,i}}{\alpha_F} \left(\sqrt{\alpha_W} + \sqrt{\alpha_F}\right)^2$$

The use of an equivalent thermal diffusivity allows the formulation of the problem with one differential equation. The single differential equation corresponds to equation (5), where α_F has been substituted by α_{EQ} and the following expression for the average regression rate (r) is obtained:

$$r = \frac{1}{H_V \rho_F}\left[\chi\left(\frac{4\,\rho_\infty\, C_p\,(T_\infty\, g\,(T_F - T_\infty))^{1/2}}{\pi}\right) d^{1/2} - \frac{\alpha_F \lambda_F (T_S - T_\infty)}{y_{S,i}\left(\sqrt{\alpha_F} + \sqrt{\alpha_W}\right)^2}\right] \qquad (9)$$

Equation (9) although simple and approximate provides an engineering tool that could be of great practical use.

BURNING RATE EXPERIMENTS

The experimental apparatus, measurement methods and experimental procedures are those described by Garo et al. (1994) and Garo (1996) and therefore will only be described briefly here. Pool burning tests of a layer of liquid fuel floating on water were conducted in a large test cell vented by natural convection. Fuel and water were placed in stainless steel pans of 0.15 m, 0.23 m, 0.30 m and 0.50 m in diameter and 0.06 m deep. Some experiments were conducted with pans of different depths to verify that the results were independent of the pan depth. The pans were placed on a load cell to measure the fuel consumption rate. The load cell had a response time of 60 ms and an accuracy within +/- 0.5 g.

The thickness of the initial fuel layer was varied from a maximum of 20 mm to a minimum thickness of 2 mm. Before each test, water was poured in the pan first followed by the fuel. The initial fuel level was established at 1 mm below the pan lip. During the combustion process the location of the fuel/water interface remained constant, therefore, the freeboard length increases during the experiment. The freeboard length changes were found to have very little effect on the steady-state burning rate.

A typical experiment involved a short unsteady ignition period followed by a steady state burning period. During steady burning the surface temperature increased slightly as the experiment progressed (lighter volatiles tend to burn off first). The steady burning period was followed by thin layer boil-over characterized by an increase in the burning rate as well as intense splashing of water and fuel. It is important to note that steady burning was followed by boilover and not extinction, therefore, no sudden decrease of the mass burning rate was observed.

The fuels used were heating oil (a mixture of hydrocarbons ranging from C_{14} to C_{21}) and crude oil (63% Kittiway, 33% Arabian Light and 4% Oural). Experiments were also conducted with weathered fuels as well as different fuel/water emulsions. Weathering refers to the evaporation of the light components of the fuel that results in significant changes of the fuel properties (density, viscosity, boiling temperature, etc.), in the laboratory it was accomplished by means of a mixer turning at 700 r.p.m. and covering 75% of the horizontal cross section of the container. Mixing was conducted for 3 different periods, 24 (~17% mass loss), 48 (~20% mass loss) and 72 hours (~21.5% mass loss). The mass loss representative of each Fuel/water emulsions were obtained by adding fixed quantities of water to the mixer and allowed to emulsify for no more than an hour. Experiments were conducted with crude oil aged for 24 hours and water contents of 10, 20, 30 and 40% in volume.

BURNING RATE EXPERIMENTAL RESULTS

Details of the experimental observations can be obtained from Garo et al. (1994, 1996) and Garo (1996) and will not be presented here. The discussion of the results will be limited to what concerns the regression rate (r). Figure 2 shows the regression rate as a function of the initial fuel thickness ($y_{S,i}$) for crude oil. The values presented here are averages but can be assumed as representative since the regression rate remained almost constant throughout the pre-boilover period. It can be observed that for $y_{S,i} > 8$ mm the regression rate is independent of the initial fuel layer thickness, instead, for $y_{S,i} < 8$ mm the regression rate decreases until no self-sustained burning can be obtained for $y_{S,i} < 2$ mm. Figure 2 also shows an increase in the regression rate with the pool diameter. It is important to note that the pool size does not seem to alter the effect of fuel layer thickness, for all pan diameters the regression rate begins to decrease for layers thinner than 8 mm.

The use of heating oil, weathered or weathered and emulsified crude oil does not seem to affect the qualitative characteristics of the curves, being a change in magnitude the only observable difference. The regression rate for heating oil is significantly lower than that corresponding to crude oil burning under equivalent conditions. The average regression velocity of weathered crude oil is also significantly slower than those characteristic of fresh oil. Experiments conducted for different weathering periods (Figure 3) showed that as the weathering time increases the regression rate decreases, with the most dramatic change occurring for the initial weathering period and with no further change observable as the weathering time extends over 72 hours.

Adding water to the fuel seems to have a similar effect on the regression rate. Figure 4 shows the average regression rate for a 15 mm layer of crude oil weathered for a period of 24 hours to which water has been added from 0 to 40% in volume. It can be observed that the average regression rate decreases as the water content increases.

The characteristic magnitudes of the regression rate correspond well to typical values found in the literature for similar fuels and pan diameters (Mudan and Croce, 1995).

DISCUSSION AND DATA CORRELATION FOR BURNING RATE

Equation (8) has been used to calculate the average regression rate (r_T) for crude oil and the results are presented in figure 5. The average regression rate matches well qualitatively and quantitatively the experimental values (r_E). Figure 5 shows, again, that the regression rate is almost

constant for $y_{S,i}$ > 8mm and decreases dramatically with the fuel layer thickness for $y_{S,i}$ < 8mm. For all data points a constant value of $\chi \approx 2.9 \times 10^{-3}$ was used. The value of ? was selected to best fit r_T with the experimental data for the constant regression rate zone.

Experimentally obtained average regression rates for heating oil, fresh crude oil, 24 hour weathered crude oil and 24 hour weathered and emulsified crude oil (20% water content) were divided by the calculated regression rate (r_E/r_T) to provide an indication of the error associated with the assumptions used to model the average regression rate, the results are presented in figure 6. The data was obtained for different pan diameters and is presented as a function of the initial fuel layer thickness ($y_{S,i}$). The predicted values are in excellent agreement with the theory for initial fuel layer thickness greater than 5 mm, for thinner fuel layers the error increases reaching, in the worst of cases, values close to 50%. This error is justifiable due to the great uncertainty present when conducting experiments with very thin fuel layers and to the average nature of the regression rates presented. The value of χ had to be adjusted to $\chi = 3.9 \times 10^{-3}$ for heating oil, to $\chi \approx 2.4 \times 10^{-3}$ for 24 hour weathered crude oil and to $\chi \approx 1.8 \times 10^{-3}$ for 24 hour weathered and emulsified crude oil (20% water content).

The heat feedback from the flame behaves in a similar way to a pool flame with no water bed, at least in the pre-boilover period. The dependence on the diameter and initial fuel layer thickness is, thus, well described by the heat flux obtained from equation (2). The use of a net heat flux as a boundary condition at the fuel surface seems also to be appropriate. It is important to note that only approximately between 0.18 % and 0.39 % of the energy released by the flame is effectively fed back to the fuel surface.

The above values of χ seem comparable to data presented by Arai et al. (1990) but no data obtained under similar experimental conditions has been found to verify these magnitudes. Experimental data on burning rate compiled by Mudan and Croce (1995) can be correlated in a similar manner to show that, for many hydrocarbons, the effective fraction of the heat of combustion that is used to evaporate the fuel is less than 1%. This information serves somehow to validate the experimental values obtained in the present work. The effective heats of combustion for the fuels studied are not well determined thus, an exact comparison between the data of reference (Mudan and Croce, 1995) and the present data could not be made.

As previously pointed out by many authors (Arai et al. (1990), Garo et al. (1994, 1996), Alramadhan et al. (1990), Brzustowski and Twardus (1982)) the water-bed acts as a heat sink. The thermal diffusivity of water is significantly larger than that of the fuel (Table 1), thus, as the fuel layer becomes thinner, the overall thermal diffusivity increases. Heat conduction through the fuel and water increases ($\dot{q}''_C$) and the overall fraction of the total heat flux ($\dot{q}''_S$) vaporizing the fuel decreases leading to a decrease in the regression rate that can eventually result in extinction ($y_{S,i}$ < 2 mm).

The data for weathered and emulsified crude oil is also well described by the predicted regression rate (figure 6). The same reasoning presented above applies for these cases, being the only difference the regression rate magnitude. Weathering and emulsification alter the thermal properties of the fuel and, thus, the magnitude of the regression rate. By changing the efficiency constant (χ) to fit the experimental data, a practical way is found to incorporate the effect of weathering and emulsification on the fuel properties. The variation of the efficiency constant as a function of the weathering period and the water content is shown on figures 7 and 8, respectively.

Figure 7 shows that initially the efficiency constant (χ) decreases quickly, followed by less significant changes till it reaches an almost constant value ($\chi \approx 2 \times 10^{-3}$). It is well known that the highly

volatile hydrocarbons will evaporate rapidly, i.e. after less than 24 hours the mass loss of hydrocarbons with boiling points below 500 K ($<C_{11}$) has reached 95% and only reaches total evaporation after 48 hours (Cox, 1995). Heavier hydrocarbons (C_{11}-C_{25}) tend to evaporate significantly slower reaching 100% mass loss only after more than 10 days. The initial fast change in fuel properties results in an abrupt decrease of χ, followed by an almost negligible change rate.

For emulsified fuels water addition will result in an almost linear decrease of χ (figure 8). The properties of the emulsified fuel change significantly with the water content and, as shown by equation 7, this will have a significant effect on the average regression rate. The way in which emulsification affects the fuel properties is not fully understood but it is well known that properties such as the density vary in an almost linear way with the water content (ρ(emulsified fuel)=(1-water fraction)ρ_F+(water fraction)ρ_W). Other properties, such as viscosity, increase in a non-linear way (Table 2).

Although the efficiency constant (χ) does not provide a real explanation to the effects of weathering and emulsification on the average regression rate it serves to quantify the flammability of the fuel independent of the pool size and fuel layer thickness. The relationship between the fuel properties and the efficiency factor goes beyond the heat transfer and evaporation mechanisms controlling the burning rate and a complete explanation will require a comprehensive study that will include the effects of weathering and emulsification on the flame chemistry and radiative feedback. An in-detail analysis of these relationships goes beyond the scope of this work.

IGNITION

The ASTM D56 Tag Closed Cup flash point tester was used to characterize the thermal properties under a controlled environment. The standard should be referenced for details of the apparatus and procedures (ASTM, 1994). Flash point is defined as the lowest temperature, at a pressure of 760 mm Hg, at which application of a test flame causes the vapors to ignite. The flash point measures the tendency of a fuel to form a combustible mixture with air under a controlled laboratory condition.

Ignition of a combustible material can be accomplished in two ways, by heating the material until ignition of the fumes occurs, spontaneous ignition, or by heating the combustible material until the mixture between the fuel and air reaches the lean flammability limit. Ignition is achieved by means of a hot spot, piloted ignition. For in-situ burning piloted ignition will be the appropriate mechanism to consider.

The mechanisms leading to gas phase ignition can be described as follows. The liquid bed is considered initially at ambient temperature, T_i . After imposing an external heat flux ($\dot{q}''_e$) the temperature of the bed rises until the surface reaches the gasification or pyrolysis temperature (T_p). The time required for the fuel surface to attain T_p is the pyrolysis time, t_p. After attaining T_p, the vapor leaves the surface mixes with the ambient oxidizer, and creates a flammable mixture near the solid surface. This period is the mixing time , t_m. If the temperature is increased until the reaction becomes self-sustained flaming ignition will occur. This is the induction time, t_i. The ignition time (t_{ig}) will be given then by

$$t_{ig}=t_p+t_m+t_i \qquad (10)$$

Introducing a pilot reduces the induction time making it negligible when compared to t_p and t_m. Furthermore, mixing can be considered as a fast process compared to heating of the fuel, therefore, pyrolysis temperatures and times are, thus, commonly referred as ignition temperature and ignition time [33] and

$$t_{ig}=t_p \tag{11}$$

and T_{ig} can be defined as T_p. In the present study the geometry will be chosen to make t_m and t_i minimal, thus $\dot{q}''_{O,p} \approx \dot{q}''_{O,ig}$ and, from equation (11), $t_p \approx t_{ig}$.

To obtain t_p the fuel and water bed are assumed as one thermally thick material. A linearized heat transfer coefficient, h, is used to describe heat transfer at the surface and all heat loss terms can be reduced to

$$\varepsilon\sigma(T^4 - T_\infty^4) + h_C(T - T_\infty) \approx h(T - T_\infty) \tag{12}$$

where h_C is the convective heat transfer coefficient, ε the emissivity of the fuel, σ the Stefan-Boltzmann constant (σ=5.67x10^{-8} W/m^2.K^4) and T_∞ the ambient temperature.

These assumptions lead to the following solution for the attainment of the pyrolysis temperature as a function of time

$$h(T_p - T_i) = \dot{q}''_e[1 - \exp(at_p)\mathrm{erfc}(at_p)] \tag{13}$$

where $a = \alpha(h/k)^2$, "α" the thermal diffusivity, "k" the thermal conductivity and both are equivalent set of properties that include the contribution of both liquids. If $\dot{q}''_e = \dot{q}''_{O,ig}$, T_p will be reached when $t \to \infty$ and a critical heat flux would be

$$\dot{q}''_{0,ig} = h(T_p - T_i) \tag{14}$$

Equation (14) predicts a linear dependency between T_p and $\dot{q}''_{0,ig}$. The flash point temperature can be used as a value for T_p but validation is necessary. For $\dot{q}''_e >> \dot{q}''_{0,ig}$ it can be assumed that $[1 - \exp(at_p)\mathrm{erfc}(\sqrt{at_p})] \approx \frac{2}{\sqrt{\pi}}(at_p)^{1/2}$ which leads to

$$t_p = \frac{\pi}{4a}\left(\frac{\dot{q}''_{O,p}}{\dot{q}''_e}\right)^2 \tag{15}$$

Equation (6) is of importance since shows that $\dot{q}''_e$ has a linear dependency on $t_p^{-1/2}$ for $\dot{q}''_e > \dot{q}''_{0,p}$, from the slope of this line the value of "a" can be determined. The experimental methodology was described by Quintiere (1981) and more recently, in the present application, by Wu et al. (2000), therefore will not be repeated here.

IGNITION EXPERIMENTAL RESULTS AND DISCUSSION

Wu et al. (2000) showed that, although the ignition delay time varies with the geometry, data converges to a unique critical heat flux for ignition. For the particular case of an oil-slick on a water bed, the water underneath might attain boiling before ignition occurs. Once boiling starts ignition of the fuel was precluded, thus, a complete description ignition can only be achieved by determination of $\dot{q}''_{0.B}$ and $\dot{q}''_{0.ig}$.

A series of tests were conducted with the two crude oils. Figure 9 shows ignition delay times for different external heat fluxes obtained for ANS crude oil, data reported by Putorti et al. (1994). It was observed that ANS crude oil in its natural state ignited at ambient temperature. When weathered, t_{ig} decreases as the heat flux increases and a linear dependency between the incident heat flux and $t_{ig}^{-1/2}$ is obtained. The intercept with the horizontal axis will provide $\dot{q}''_{0.ig}$ showing that $\dot{q}''_{0.ig}$ increases with weathering. It can be observed that the slopes remain invariant with the weathering level. The $\dot{q}''_{0.ig}$ value corresponding to the data reported by Putorti et al (1994) fits well with the present work. As previously mentioned the different experimental conditions account for the difference in slope.

As demonstrated by equation (6) the slope of the line fit to the data presented in figures 9 provides the thermal property, "a", of the fuel. Figure 9 shows that the slope remains invariant with the mass loss due to weathering. This proves that although the ignition event is controlled by the most volatile fractions of the crude oil, thus is affected by weathering, the heating process is determined by the heavier fractions, thus invariant with weathering. The critical heat flux for ignition ($\dot{q}''_{O,ig}$) as obtained from figure 9 is presented in figure 10. Results are presented for Cook Inlet and ANS crude oils. Figure 10 shows a discrepancy between the critical heat flux for ignition for 3 mm as opposed to almost identical values obtained for 8 and 15 mm layers. The effect of fuel layer thickness was mostly manifested on the curves being truncated by boiling before attaining $\dot{q}''_{O,ig}$. Based on the values for $\dot{q}''_{O,ig}$ ANS crude oil was observed to be more prompt to ignition than Cook Inlet crude oil. Cook inlet ignited without an external heat flux for a mass loss rate smaller than 10 % and ANS crude oil for a mass loss smaller than 7%. The results presented are representative of all other cases studied.

The flash point for the crude oils as a function of the mass loss are presented in figure 11. Each point in the figure represents the average of 10 tests conducted in accordance with ASTM D56 standard (ASTM, 1994). Flash points show a linear dependence on the level of evaporation for both crude oils. More importantly, the flash points for ANS crude oils are significantly higher than the Cook Inlet crude.

Figure 12 shows that the flash point temperature has a linear dependency with the critical heat flux for ignition ($\dot{q}''_{o,ig}$), as predicted by equation (14). The line fits converge to the ambient temperature (20^oC) for $\dot{q}''_{o,ig} = 0$. This shows that the flash point temperature can be used as characteristic ignition temperature. Furthermore, by means of equation (14) the global heat transfer coefficient can be evaluated and corresponds to the slope of the line fit.

If the global heat transfer coefficient (h) is known, and "a" is extracted from the ignition delay time, a "fire property," the product of the thermal conductivity, the density and the specific heat capacity ($k\rho C$) can be obtained ($(k\rho C)=h^2/a$).

CONCLUSIONS

A simple one dimensional heat conduction model has been used to describe the regression rate of a fuel layer on a water bed. Crude and heating oil have been used to test the validity of the phenomenological model for a wide range of conditions. The model describes accurately the regression rate for fuel layers thicker than 2 mm. Deviations from the predicted values arise from the assumptions used in the model and from the uncertainties in the experimental results for $y_{S,i} < 5$ mm. The model accurately describes for all conditions the dependency of the average regression rate on the pool diameter and initial fuel layer thickness.

A value for an efficiency constant $0.001 < \chi < 0.004$ is obtained under all experimental conditions. The efficiency constant represents the fraction of the energy released at the flame that will be retained by the fuel/water. For the conditions studied the efficiency constant does not depend on the pool diameter or the initial fuel layer thickness being only affected by the fuel characteristics. Determination of the range of validity of this statement requires further experimentation.

Weathering and emulsification affect the fuel properties and, thus, the regression rate. An increase in the weathering period and in the water content results in a decrease in the regression rate. Although weathering and emulsification affect the fuel properties, a practical way of incorporating this effect is by introducing the dependency in the efficiency constant. It was found that after a sudden decrease, the efficiency constant is almost independent of the weathering period ($t > 36$ hours). A linear decrease of the efficiency constant was found with the water content.

The propensity of a crude oil to ignite can be characterized by three different parameters: The critical heat flux for ignition ($\dot{q}''_{o,ig} \approx \dot{q}''_{0,P}$), the critical heat flux for boiling ($\dot{q}''_{o,B}$) and the thermal "fire property" of the fuel ($k\rho C$).

This approach provides an engineering approximation to the complex process of in-situ burning of oils in a water-bed. The parameters extracted provide a relative quantification of the burning efficiency of the fuel. This approach does not provide a description of the burning scenario but focuses on the fuel, therefore can serve to provide relative rankings between different fuels and fuels under different levels of weathering or emulsification. This approach does not provide a substitute to large scale testing but its use will result in a significant reduction of the necessary large-scale tests necessary to assess the viability of in-situ burning as a counter-measure to an oil spill.

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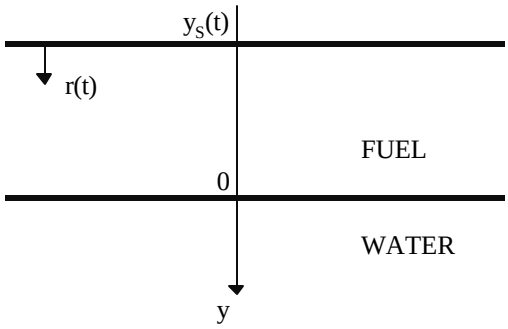

Figure 1. Schematic of the problem studied

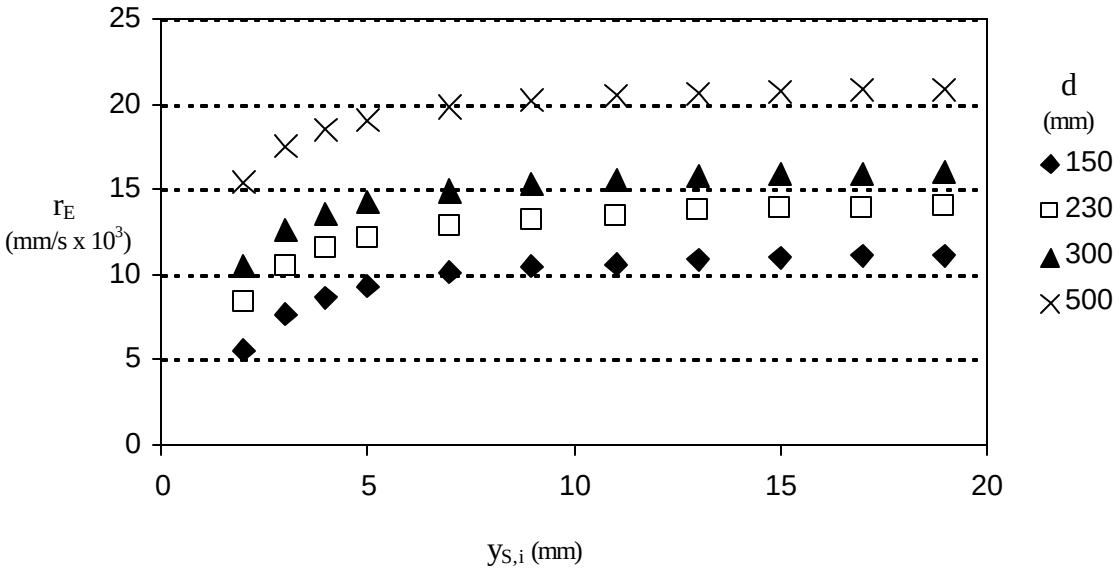

Figure 2. Regression rate as a function of initial fuel layer thickness for different pool diameters (experimental).

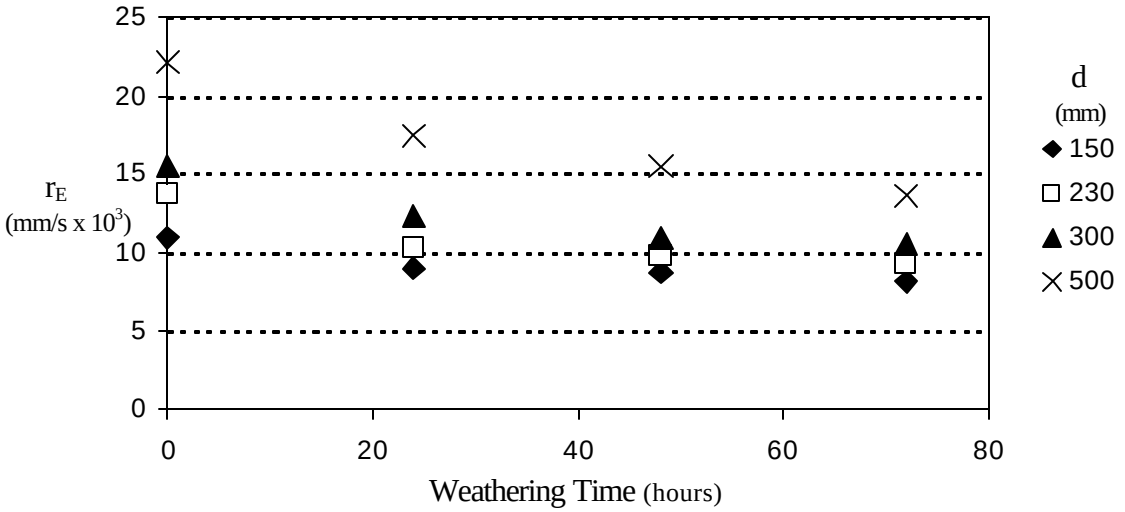

Figure 3. **Regression rate as a function of the weathering period for different pool diameters.**

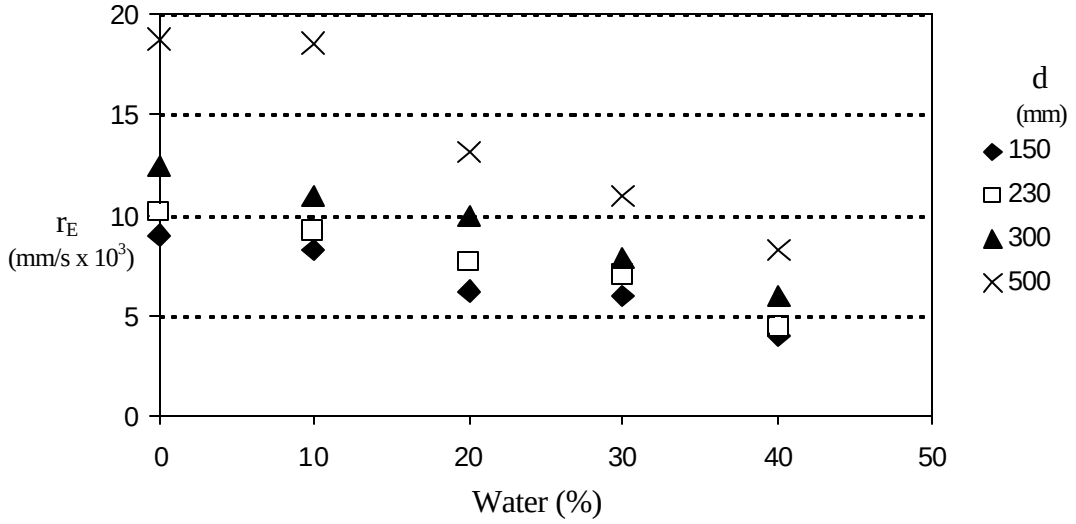

Figure 4. **Regression rate as a function of the water content for different pool diameters.**

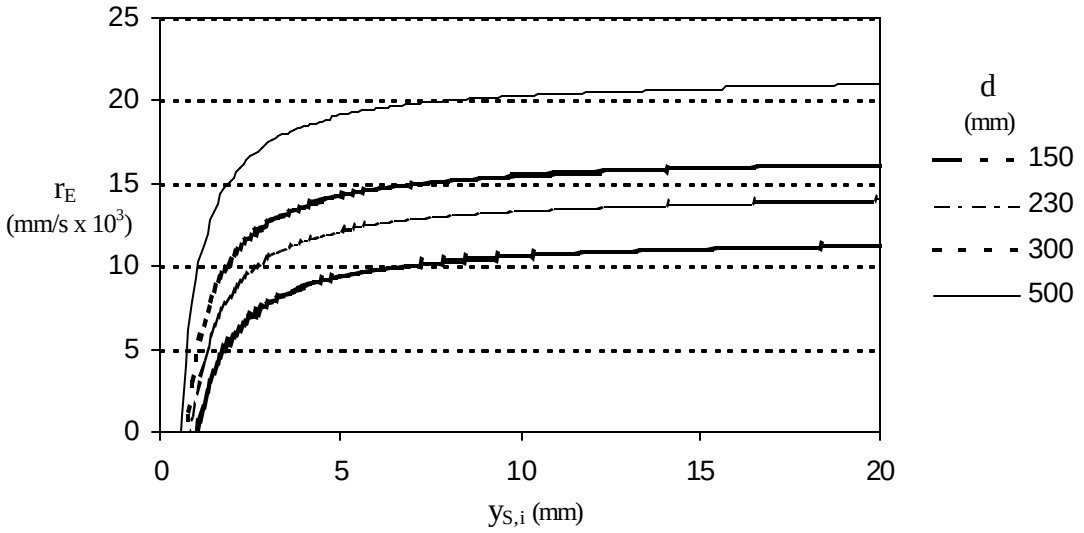

Figure 5. Regression rate as a function of initial fuel layer thickness for different pool diameters (calculated).

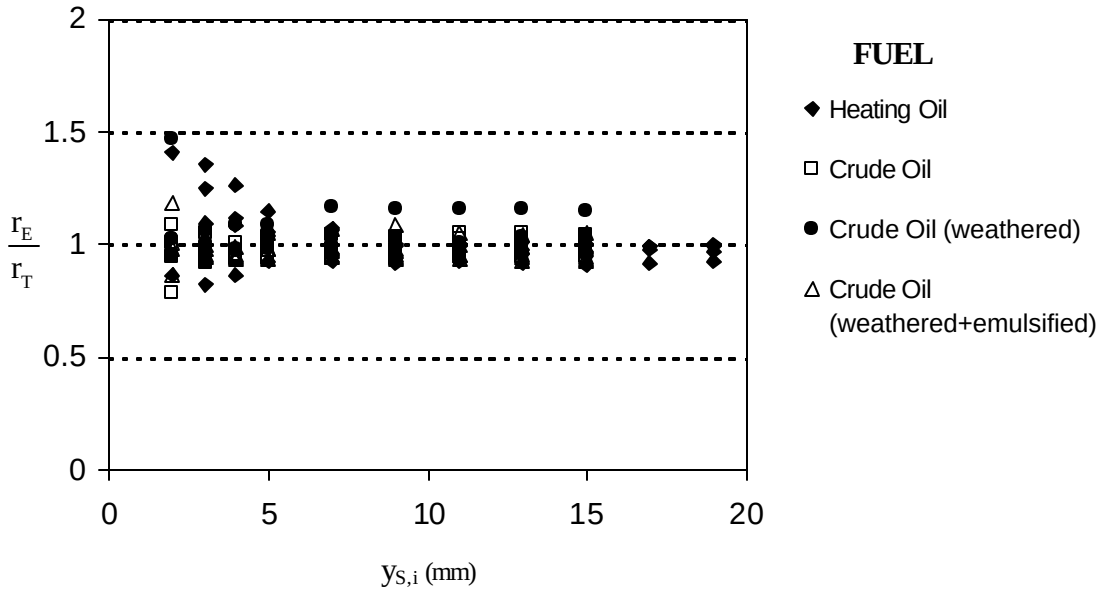

Figure 6. Comparison between experimental (r_E) and calculated (r_T) regression rates.

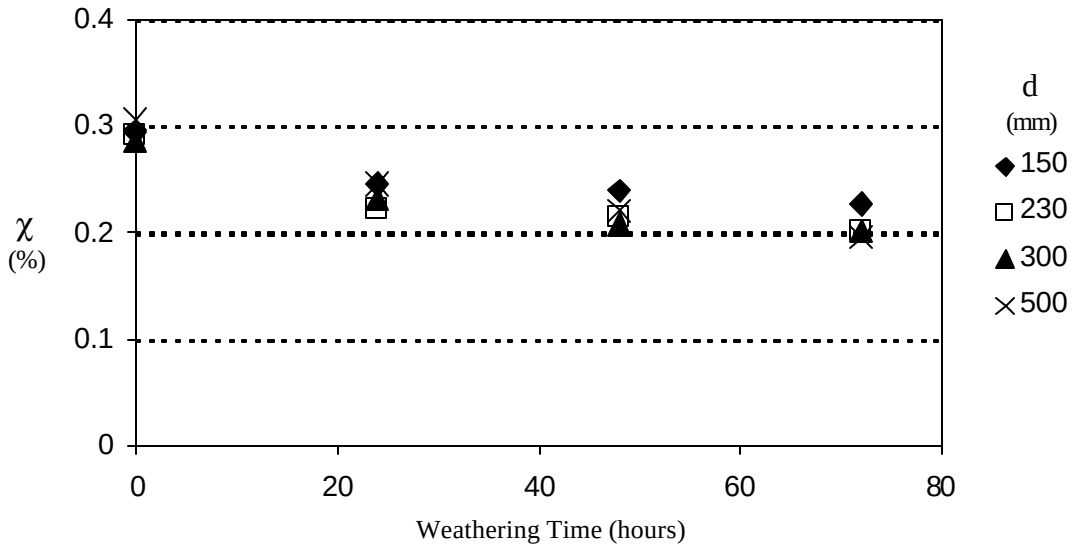

Figure 7. Efficiency constant as a function of the weathering period for crude oil.

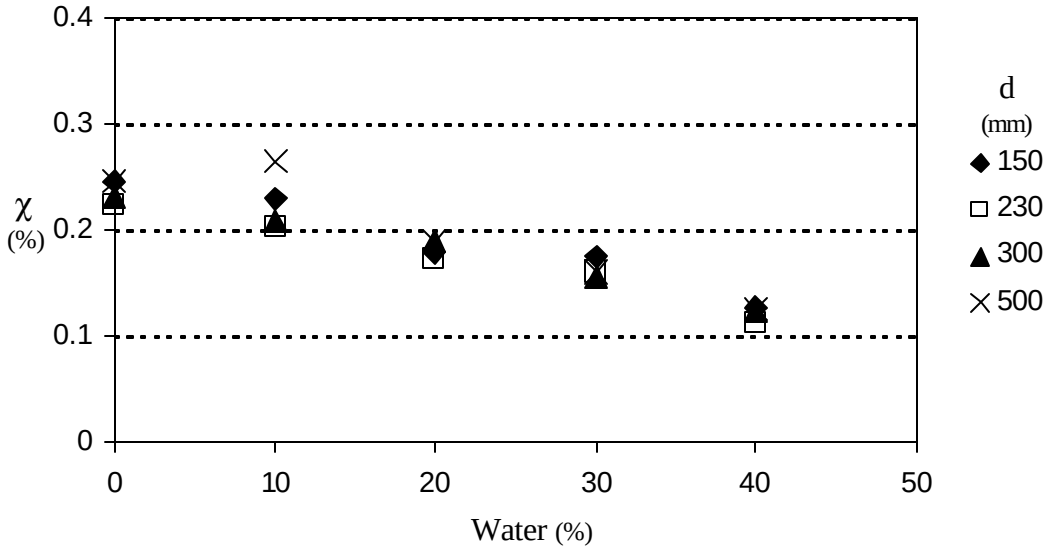

Figure 8. Efficiency constant as a function of the water content period for emulsified crude oil (weathered 24 hours).

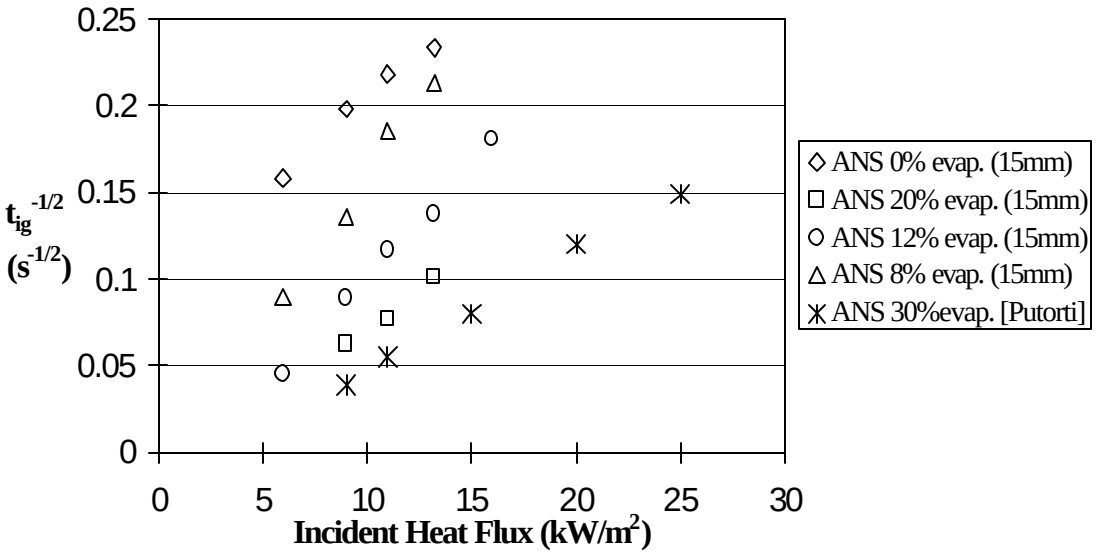

Figure 9, ANS Crude Oil Ignition Delay Time for Various Levels of Evaporation.

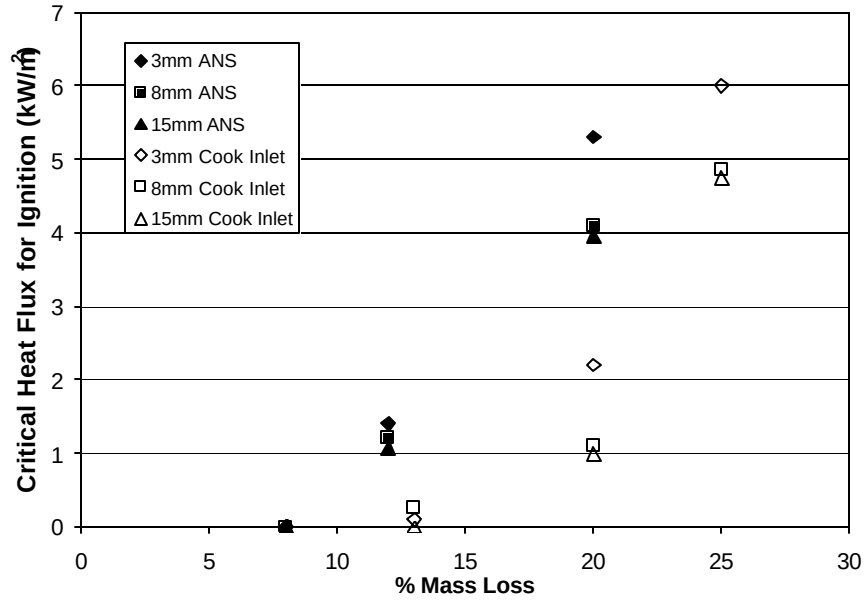

Figure 10. $\dot{q}''_{o,ig}$ **for ANS and Cook Inlet Crude Oils at Various Fuel Layer Thickness.**

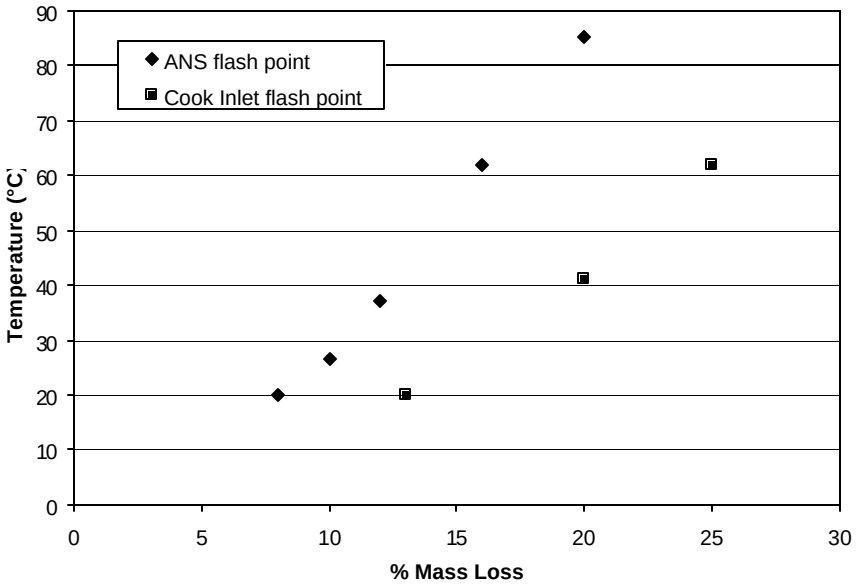

Figure 11. ASTM D56 Closed Cup Flash Point Tests for ANS and Cook Inlet.

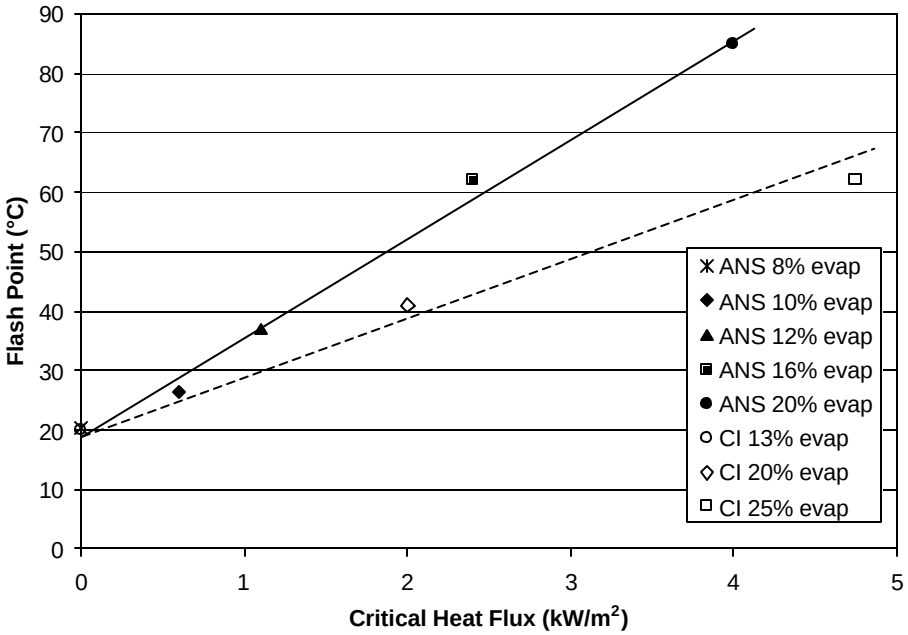

Figure 12. Flash Points at Various Levels of Weathering.

	T_S	ν ($x10^4$) (at 20°C) (m^2/s)	H_V (kJ/kg)	λ (at 20°C) (W/m.K)	ρ (at 20°C) (kg/m^3)	C_p (at 20°C) (kJ/kg.K)	α ($x10^7$) (at 20°C) (m^2/s)
Crude Oil	478	9.83	250	0.132	845	2.30	0.679
Heating Oil	538	5.31	377	0.137	844	1.90	0.854
Air	-	0.159	-	0.026	1.16	1.00	225.0
Water	373	1.00	2257	0.590	998	4.18	1.414

Table 1. Properties.

Water Content	Density kg/m^3	Viscosity m^2/s (x 10^6)
0 %	876	0.2454
10 %	887	0.4386
20 %	902	0.7561
30 %	921	1.6145
40 %	936	2.6987

Table 2. Properties of crude oil weathered for 24 hours.